

SODA-LIME-SILICA GLASS COMPOSITION, ESPECIALLY FOR PRODUCING SUBSTRATES.

5 The present invention relates to glass compositions that can be converted into a glass ribbon, especially by the « float » process, from which ribbon heat-resistant glass plates can be cut. These plates can be used especially for the production of substrates used in the manufacture of emissive displays, such as plasma displays, electroluminescent displays and cold-cathode displays or FEDs (Field Emission Displays), or in the
10 manufacture of fire-resistant glazing.

The glass employed for producing such substrates is a glass belonging to the family of soda-lime-silica glasses, commonly used for forming the glazing intended for buildings or for motor vehicles. Although this type of glass is satisfactory as regards chemical resistance, flatness and the defects that it contains, the level of performance in
15 terms of ability to undergo yellowing proves, however, to be insufficient for the intended application.

In the manufacture of emissive displays, the substrate is subjected to several treatments for the purpose of stabilizing its dimensions and for attaching a series of layers of various compounds, such as enamels, that are deposited on its surface. To attach these
20 layers of variable thicknesses, the substrate is in general heat treated at a temperature above 550°C. In this regard, it is important to ensure that the expansion coefficient of the glass used is of the same order of magnitude as that of the compounds deposited on its surface so as to prevent the appearance of crazing. Although soda-lime-silica glass generally has a suitable expansion coefficient, its temperature withstand capability is,
25 however, insufficient and it is necessary to place it on a ground slab to avoid any deformation during the heat treatments.

Moreover, it has been observed that substrates made of soda-lime-silica glass bearing heat-treated silver-based layers have a tendency to develop a yellow coloration. This yellowing phenomenon is attributed to the migration of Ag⁺ ions into the glass, which
30 ions are then reduced to the form of colloidal Ag⁰ particles that absorb light in the wavelength range from 390 to 420 nanometers. The yellowing of the glass is a contributory factor in degrading the quality of the image.

The glasses used for the manufacture of fire-resistant glazing belonging to the category of borosilicate glasses. Such glasses, which exhibit good resistance to heat and

heat shocks, are characterized by a relatively low expansion coefficient. As a result, the mechanical strength of this type of glass cannot be significantly improved by thermal toughening as the development of high stresses in the glass is not allowed.

Glass compositions for obtaining plates or substrates with virtually zero deformation during heat treatments of around 550 to 600°C and capable of undergoing thermal toughening are disclosed in WO-A-96/11887. These are glass compositions having the desired properties for plasma displays, which use little or no alumina Al_2O_3 (0 to 18 %), having a high content (6.5 to 20 %) of zirconia ZrO_2 and an SiO_2 content not exceeding 63%.

Compositions for providing thermally stable substrates which combine alumina (0 to 5%) and zirconia (5 to 10%) are also disclosed in FR-A-2 578 550.

However, with one or other of the compositions, the glass yellowing phenomenon persists. There is therefore a need for improved glass compositions that make it possible to obtain glasses having the lowest possible degree of yellowing.

The object of the present invention is to propose a glass composition for manufacturing a plate or a substrate which exhibits improved resistance to yellowing and retains the abovementioned properties, in particular a thermal expansion coefficient α at least equivalent to that of known soda-lime-silica glasses.

The subject of the invention is a glass composition intended for the manufacture of thermally stable substrates or plates that comprises the constituents given below, in the following proportions by weight :

| | | |
|----|-----------|-----------|
| | SiO_2 | 67 - 75 % |
| | Al_2O_3 | 0.5 - 1 % |
| | ZrO_2 | 2 - 7 % |
| 25 | Na_2O | 2 - 9 % |
| | K_2O | 4 - 11 % |
| | MgO | 0 - 5 % |
| | CaO | 5 - 10 % |
| | SrO | 5 - 12 % |
| 30 | BaO | 0 - 3 % |
| | B_2O_3 | 0 - 3 % |
| | Li_2O | 0 - 2 % |

with the relationships :

$$Na_2O + K_2O > 10 \%$$



and said composition having a thermal expansion coefficient between 80 and $90 \times 10^{-7}/^\circ\text{C}$, especially less than $85 \times 10^{-7}/^\circ\text{C}$, and preferably between 81 and $84 \times 10^{-7}/^\circ\text{C}$.

The substrates or plates obtained from the compositions according to the invention are capable of undergoing the heat treatments needed for their application, for example as a plasma display, and have a lower degree of yellowing compared with soda-lime-silica glasses. The improvement in aging of the glass, consisting in limiting the appearance of yellow coloration, is not, however, obtained to the detriment of the other properties of the glass.

The reduction in yellowing stems from the choice of a high SiO_2 content (equal or greater than 67 %), a very low Al_2O_3 content (0.5 to 1 %) and a low ZrO_2 content (2 to 7 %). By virtue of the combination of the constituents, as results from the definition of the invention, it is possible to obtain glasses having a thermal expansion coefficient that remains the same order of magnitude as that of a conventional soda-lime-silica glass, namely between 80 and $90 \times 10^{-7}/^\circ\text{C}$, especially less than $85 \times 10^{-7}/^\circ\text{C}$, and preferably between 81 and $84 \times 10^{-7}/^\circ\text{C}$ measured at a temperature between 20 and 300°C.

The combination of the aforementioned constituents also makes it possible to obtain glasses having a strain point above 570°C, preferably 580°C, which temperature is at least about 70°C higher than that of a conventional soda-lime-silica glass. It is known that the glass no longer exhibits any viscous behavior above the strain point corresponding to the temperature at which the glass has a viscosity of the order of $10^{14.5}$ poise. Thus, the strain point is a useful reference point for evaluating the temperature withstand capability of a glass. The strain point of the glasses according to the invention is comparable to that obtained for other known glasses for producing displays (see WO 96/11 887 and FR 2 758 550).

The glasses according to the invention have in general a density at 25°C of less than 3, preferably around 2.7, similar to that of the existing glasses used for manufacturing displays.

The glasses according to the invention are well suited to the melting techniques associated with the float process, in which the glass floats on a bath of molten metal, especially tin. They cause only very slight corrosion of the refractories, of the AZS (alumina-zirconia-silica) type, that are normally employed in this type of furnace.

The glasses according to the invention can be easily melted and converted into glass ribbon at temperatures of the same order as those used for the manufacture of a conventional soda-lime-silica glass.

Thus, they generally have a liquidus temperature T_{liq} corresponding to the melting point of the batch materials of at most 1180°C, especially between 1130 and 1170°C. These glasses also have a temperature of at least 1160°C, especially between 1160 and 1200°C at which the viscosity η (in poise) is such that $\log \eta = 3.5$. For a person skilled in the art, this temperature corresponds to the ideal viscosity for forming the glass.

The compositions according to the invention have a “working range”, defined by the temperature difference $T_{\log \eta = 3.5} - T_{liq}$ (corresponding to the temperature range allowing the glass to be melted and formed), of at least 10 to 30°C. This working range, although narrow, is sufficient for ensuring proper forming without a major risk especially in the operation of the furnace.

The role of the constituents employed in the glass composition according to the invention is defined below.

SiO_2 plays an essential role. Its content is necessarily equal to or greater than 67 %, without however exceeding 75 % ; above this, the melting of the charge and the refining of the glass require high temperatures, which cause premature wear of the furnace refractories. Below 67% by weight of silica, the performance of the glass, especially in terms of yellowing, is reduced. The glasses that are best suited to the conditions of floating on a bath of molten metal, and have the best properties, contain between 67 and 71% SiO_2 .

Alumina acts as a stabilizer. It contributes to increasing the chemical resistance of the glass and the strain point.

ZrO_2 also acts as a stabilizer. This oxide increases the chemical resistance of the glass to a certain extent and helps to increase the strain point. The percentage of ZrO_2 generally does not exceed 7% so as not to penalize the melting operation. Although this oxide is difficult to melt, it has the advantage of increasing only moderately the viscosity of the glasses according to the invention at high temperatures, unlike the other oxides such as silica or alumina. The use of the ZrO_2 makes it possible to avoid introducing oxides such as B_2O_3 into these glasses or to increase the amount of alkali metal oxides, one of the effects of these oxides being to reduce the viscosity of the glass.

Alumina and zirconia fulfill quite similar roles : the sum of the Al_2O_3 and ZrO_2 contents is preferably less than 6 %.

The oxides Na_2O and K_2O allow the melting point of the glasses and the viscosity at high temperatures to be maintained within the abovementioned limits. To do this, the sum of these oxides remains equal to or greater than 10 %, preferably between 10 and 15 %. Compared with a conventional soda-lime-silica glass, the presence of Na_2O and K_2O makes it possible for their chemical resistance, especially their hydrolytic resistance, and their resistivity to be considerably increased. When it is desired to increase the overall content of Na_2O and K_2O , it is preferable that it be the K_2O content that increases, as this allows the glass to be thinned without excessively lowering the strain point. Advantageously, the weight ratio of the Na_2O content to the K_2O content is less than or equal to 0.7.

The alkaline-earth oxides have the overall effect of raising the strain point : as a general rule, their total content, especially the total content of MgO , CaO , SrO , and BaO , is greater than 12 %, preferably greater than or equal to 15 %.

Above about 15 %, the ability of the glasses to devitrify increases and may become incompatible with the conditions for manufacturing the glass by floating on a bath of molten metal. It is essentially CaO and MgO that allow the value of the strain point to be increased.

To maintain devitrification of the glasses within acceptable limits, the CaO and MgO weight contents do not exceed 5 % and 10 %, respectively.

BaO and SrO are used to increase the chemical resistance of the glass and BaO also has the effect of reducing the melting point and the viscosity at high temperatures.

Boron oxide, B_2O_3 , is optional. This network-former oxide may be added to or substituted for SiO_2 . It reduces the melting point of the charge and the viscosity of the glass at high temperatures. It also reduces the ability of the glass to devitrify, particularly by preventing a rise in the liquidus temperature.

Lithium oxide, Li_2O , is also optional. It may be introduced into the glass in an amount not exceeding 2 % and has the effect in particular of lowering the melting point.

Overall, the melting of the glasses according to the invention remains within acceptable temperature limits provided that the sum of the SiO_2 , Al_2O_3 and ZrO_2 contents remains equal to or less than 83 %, preferably 80 %. The term "acceptable limits" is understood to mean here that the temperature of the glass corresponding to a viscosity η , such that $\log \eta = 2$ does not exceed about 1560°C and preferably 1550°C .

The preferred glass compositions according to the invention comprise the constituents below in the following proportions :

| | | |
|----|--------------------|-----------|
| | <chem>SiO2</chem> | 67 - 75 % |
| | <chem>Al2O3</chem> | 0.5 - 1 % |
| | <chem>ZrO2</chem> | 2 - 5 % |
| | <chem>Na2O</chem> | 2 - 4 % |
| 5 | <chem>K2O</chem> | 7 - 11 % |
| | <chem>MgO</chem> | 0 - 2 % |
| | <chem>CaO</chem> | 6 - 10 % |
| | <chem>SrO</chem> | 6 - 12 % |
| | <chem>BaO</chem> | 0 - 2 % |
| 10 | <chem>B2O3</chem> | 0 - 3 % |
| | <chem>Li2O</chem> | 0 - 2 %. |

The glass compositions according to the invention can be used for the manufacture of heat-resistant plates, especially for forming substrates for plasma, electroluminescent or field-emission displays. These substrates may be obtained by cutting 15 glass sheets from a continuous glass ribbon obtained by floating the glass on a bath of molten metal. They may have a glass thickness that varies from 0.5 mm to 10 mm.

These plates may also be used for the manufacture of fire-resistant glazing, again especially obtained by cutting them from a ribbon of floated glass.

The advantages afforded by the compositions according to the invention will be 20 more fully appreciated through the illustrative examples given in Table 1 appended hereto.

Examples 1 to 4 describe glass compositions according to the invention. The glass of Example 5 corresponds to a conventional soda-lime-silica glass composition used to manufacture a glass ribbon by the float process. The glass of Example 6 is a glass sold under the name PD200 by Asahi, suitable for the production of emissive displays.

25 This table gives, for each example, the weight contents and the values of the properties of the glasses obtained, namely the strain point, the thermal expansion coefficient $\alpha_{25-300^\circ\text{C}}$, b^* , $T_{\text{liq}} - T_{\log \eta=3.5}$, $T_{\log \eta=2}$ and density.

The value of b^* is representative of the degree of yellowing of the glass. It is measured in the following manner :

30 A film of metallic silver is deposited on the surface of the glass using the "sputtering" method. The glass is then heated to 580°C at the rate of 10°C/min, maintained at this temperature for 30 min and then cooled to room temperature at the rate of 5°C/min. The glass is immersed in an HNO3 solution in order to remove the silver film. The

chromatic coordinate b^* is measured under illuminant D₆₅ taking the colorimetric reference observer described by the Commission Internationale de l'Eclairage (CIE) 1931.

The other properties were measured using methods well known to those skilled in the art.

5 As Examples 1 to 4 show, the degree of yellowing after heat treatment of the glasses according to the invention is markedly lower than that of the soda-lime-silica glass of Example 5 or of the display glass of Example 6.

It should be noted that the coefficient α retains a satisfactory value, of greater than $80 \times 10^{-7}/^\circ\text{C}$, comparable to the aforementioned reference glasses.

10 The strain point of the glasses according to the invention is much higher than that of the soda-lime-silica glass and is improved over the display glass.

Moreover, the glasses according to the invention are manufactured under the float process conditions without any problems, whether as regards melting in the furnace or floating on the bath of molten metal, given that the difference between the temperature

15 $T_{\log \eta} = 3.5$ and the liquidus temperature T_{liq} remains positive.

8
Table 1

| | Ex. 1 | Ex. 2 | Ex. 3 | Ex. 4 | Ex. 5 | Ex. 6 |
|--|-----------|-----------|-----------|-----------|-------|-------|
| SiO ₂ | 67.5 | 67.5 | 67.5 | 67.5 | 71.4 | 58.0 |
| Al ₂ O ₃ | 0.50 | 0.50 | 0.50 | 0.50 | 0.60 | 6.75 |
| ZrO ₂ | 2 | 2 | 2 | 2 | 0 | 2.85 |
| Na ₂ O | 2.0 | 4.0 | 3.0 | 3.0 | 14.0 | 4.1 |
| K ₂ O | 10.0 | 8.0 | 10.0 | 10.0 | 0 | 6.4 |
| MgO | 0 | 0 | 0 | 0 | 4 | 2.0 |
| CaO | 9 | 9 | 8 | 10 | 9.6 | 4.95 |
| SrO | 9 | 9 | 9 | 7 | 0 | 7.05 |
| BaO | 0 | 0 | 0 | 0 | 0 | 8 |
| Strain point (°C) | 592 | 584 | 586 | 586 | 505 | 581 |
| α ($\times 10^{-7}/^{\circ}\text{C}$) | 81.32 | 82.72 | 83.92 | 83.60 | 89.00 | 83.00 |
| b* | ≤ 2 | ≤ 2 | ≤ 2 | ≤ 2 | 8.2 | 6.4 |
| $T_{\text{liq}} - T_{\log \eta = 3.5}$ (°C) | ≥ 10 | ≥ 10 | ≥ 10 | ≥ 10 | 65 | 155 |
| $T_{\log \eta = 2}$ (°C) | 1559 | 1527 | 1558 | 1543 | 1450 | 1545 |
| Density | 2.71 | 2.71 | 2.71 | 2.70 | 2.52 | 2.76 |